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A METALLURGICAL ROUTE TO SOLAR-GRADE SILICON

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ABSTRACT

The aim of the process is to produce a silicon for crystallization into ingots that can be sliced to wafers for processing into photovoltaic cells. The specifications of the product are:

		Present	Potential
B	ppmw	< 1	< 1
P	"	< 1	< 1
C	"	< 50(?)	< 1
Ca	"	< 10	< 10
Al	"	< 10	< 0.1
Other metals	"	< 10	< 0.001

If the potential purity can be realized, the silicon will also be applicable for ribbon pulling techniques where the purification during crystallization is negligible.

The process consists of several steps: Selection and purification of raw materials, carbothermic reduction of silica, ladle treatment, casting, crushing, leaching and remelting. The leaching step is crucial for high purity, and the obtainable purity is determined by the solidification before leaching. The most difficult specifications to fulfil are the low contents of boron, phosphorus and carbon. Boron and phosphorus can be excluded from the raw materials, but the carbothermic reduction will unavoidably saturate the silicon with carbon at high temperature. During cooling carbon will precipitate as silicon carbide crystals, which will be very harmful in solar cells.

The cost of this solar silicon will depend strongly on the scale of production. It is as yet premature to give exact figures, but with a scale of some thousand tons per year, the cost will be only a few times the cost of ordinary metallurgical silicon.

INTRODUCTION

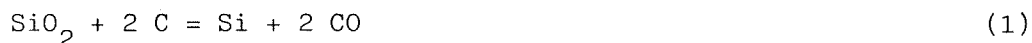
The carbothermic process is potentially the cheapest process for silicon production, but the purity of the typical metallurgical silicon is far below the specifications of a solar silicon for use in a Bridgman or similar crystallization.

	Metallurgical grade	Solar grade
	Typical content	Tentative specifications
B	30 ppmw	1 ppmw
P	50 "	0.3 "
C	250 "	No SiC precipitate
Metals	6000 "	10 ppmw

The problem is then to improve the metallurgical process to give the solar grade silicon. This paper describes one solution to this problem. A more detailed description, including references to several other approaches, is given elsewhere [1]. The work was done by Exxon Research and Engineering Company and Elkem a/s in a joint project on low cost silicon for solar cells. The project was partly based on a research programme run at Dow Corning by Hunt and Dosaj [2].

SURVEY OF THE CARBOTHERMIC PROCESS

A complete carbothermic route to solar silicon is sketched in Figure 1. The smelting step has an overall reaction



The detailed reaction mechanism is, however, more complex. The recovery of the impurities is high, and one can as a first approximation assume that all the impurities in the raw materials will be recovered in the silicon.

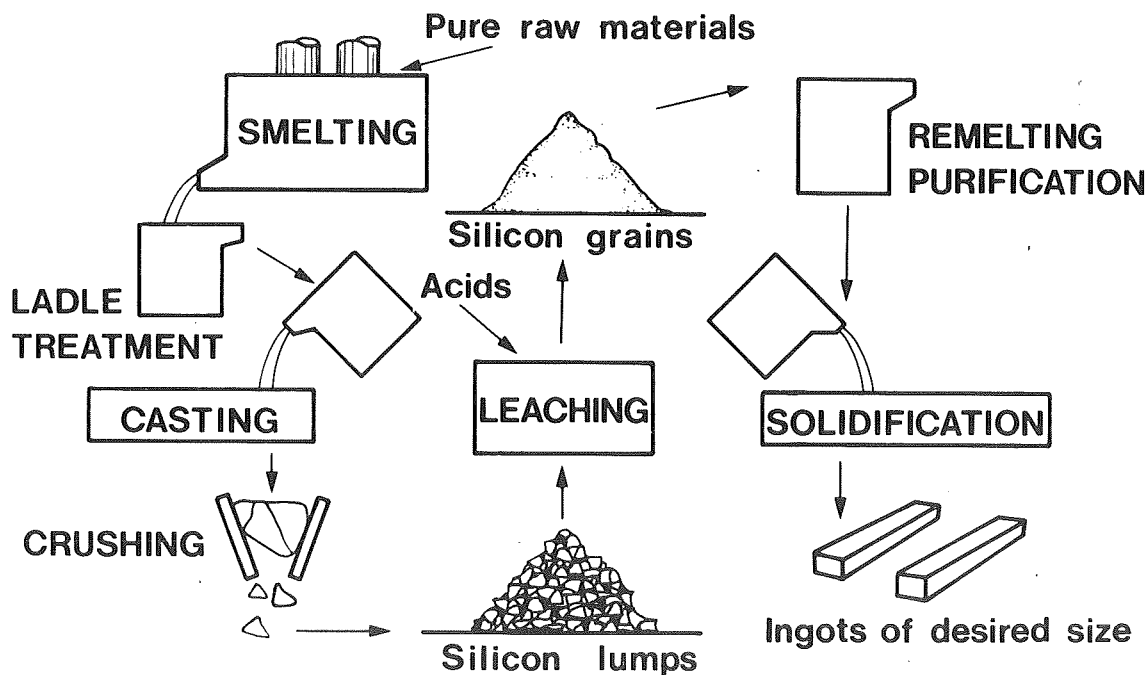
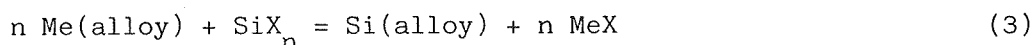


Figure 1.
Survey of the carbothermic route to metallurgical silicon

The molten silicon from the smelting furnace can be purified in the ladle. Separate impurity phases, as silicates and silicon carbide, will partly stick to the lining of the ladle, and some can be removed in a filtering step. Impurities (Me) dissolved in the molten silicon can be attacked by a purifying agent (X):



This exchange type of reaction limits the possibilities of ladle purification to elements less noble than silicon, that is in practice to aluminium and calcium. Important impurities like iron and titanium cannot be removed significantly. A thorough discussion of the refining of molten silicon has recently been given by Tuset [3].

The molten silicon is cast and crushed to lumps, which are leached in acids. If the silicon contains sufficient calcium (or other suitable elements), the lumps will disintegrate to millimeter-sized silicon grains, while most of the impurities are dissolved. The grains are remelted and solidified to crystalline ingots for slicing to wafers.

Boron and phosphorus are, as will be seen later, only weakly removed by this process. Therefore, it is essential to have a low boron and phosphorus content in the raw materials.

In this process the leaching step is crucial for obtaining a less than 10 ppmw content of the metallic impurities. Alternatively one could have started with extremely pure or purified raw materials, but a smelting furnace operation adding less than 10 ppmw metallic impurities, will probably be rather difficult and more expensive than leaching.

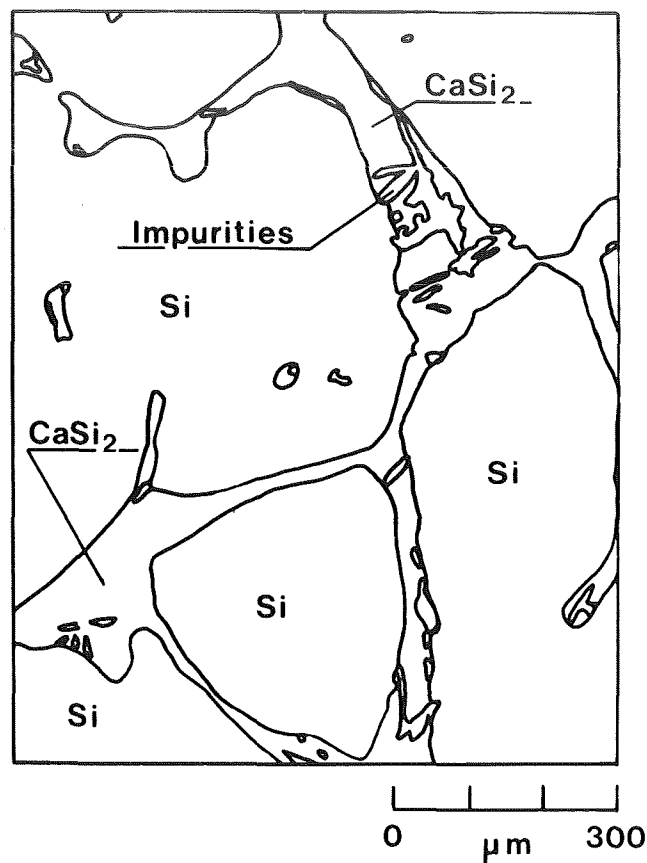
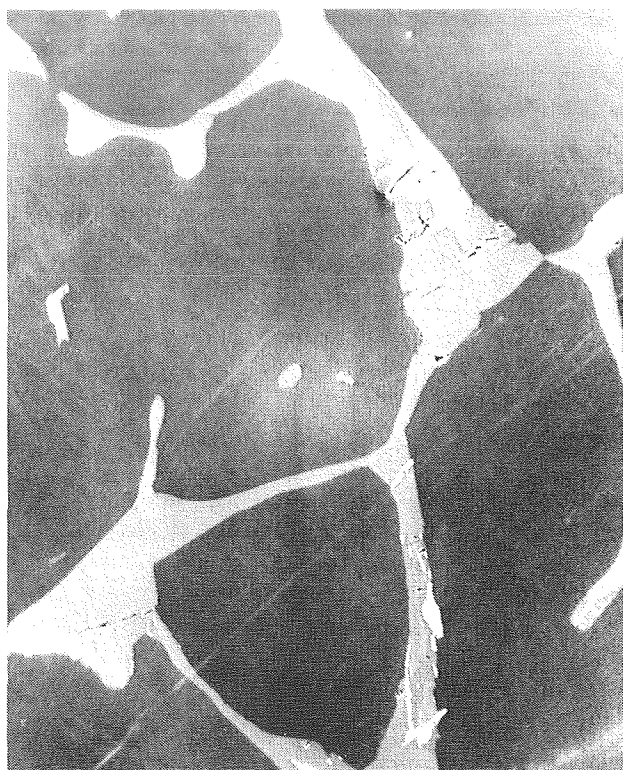
THE LEACHING STEP

The Elkem leaching process

Elkem has developed a modification of the general leaching process that makes it suitable for production of high purity silicon [4]. Silicon containing a few per cent calcium is cast, cooled slowly and then crushed into lumps around 5 cm in size. The lumps are treated with an aqueous mixture of hydrochloric acid with ferric chloride and disintegrate giving fairly pure silicon crystals of a size below 2 mm. These crystals are then further purified with hydrofluoric acid in combination with some oxidizing agent.

Chemical interpretation of the leaching

The leaching can be understood from the microstructure of the leaching alloy. A scanning electron micrograph is shown in Figure 2. Fairly large silicon crystals are separated by the phase calcium disilicide, CaSi_2 . Other impurities are concentrated as small grains within the calcium disilicide phase.



Photograph: A. G. Forwald

Figure 2.

Scanning electron micrograph of the leaching alloy. The micrograph gives an indication of the chemical composition: The darker a phase, the lower the mean atomic mass. The amounts and compositions of the impurity phases are strongly dependent upon the composition of the leaching alloy. In the present sample compositions close to the following formulas were found: FeSi_2 , AlSiCa , FeAlSiCa , FeSi(Ti,V) .

This structure should be expected from the phase diagrams of the systems Ca-Si and Ca-Si-Me (Figure 3). When an alloy A of silicon, calcium and a small amount of a third element Me is cooled, fairly pure silicon crystals are precipitated, and the composition of the melt changes along the crystallization path AE. At E the phase calcium disilicide starts precipitating eutectically together with the silicon phase, and with further cooling more solid precipitates until the alloy is completely solidified at a eutectic or peritectic point. In a technical process Me is replaced by a mixture of several elements, corresponding to a multicomponent phase diagram. The behaviour will still be analogous to the simpler three component system discussed above, and the type of alloy structure shown in Figure 2 will be formed. A condition for this crystallization sequence is a sufficiently high calcium content in the leaching alloy. Then all the impurity phases will occur within the calcium disilicide phase.

When the alloy is treated with hydrochloric acid and ferric chloride, the calcium disilicide reacts and swells. The lumps of calcium-containing silicon

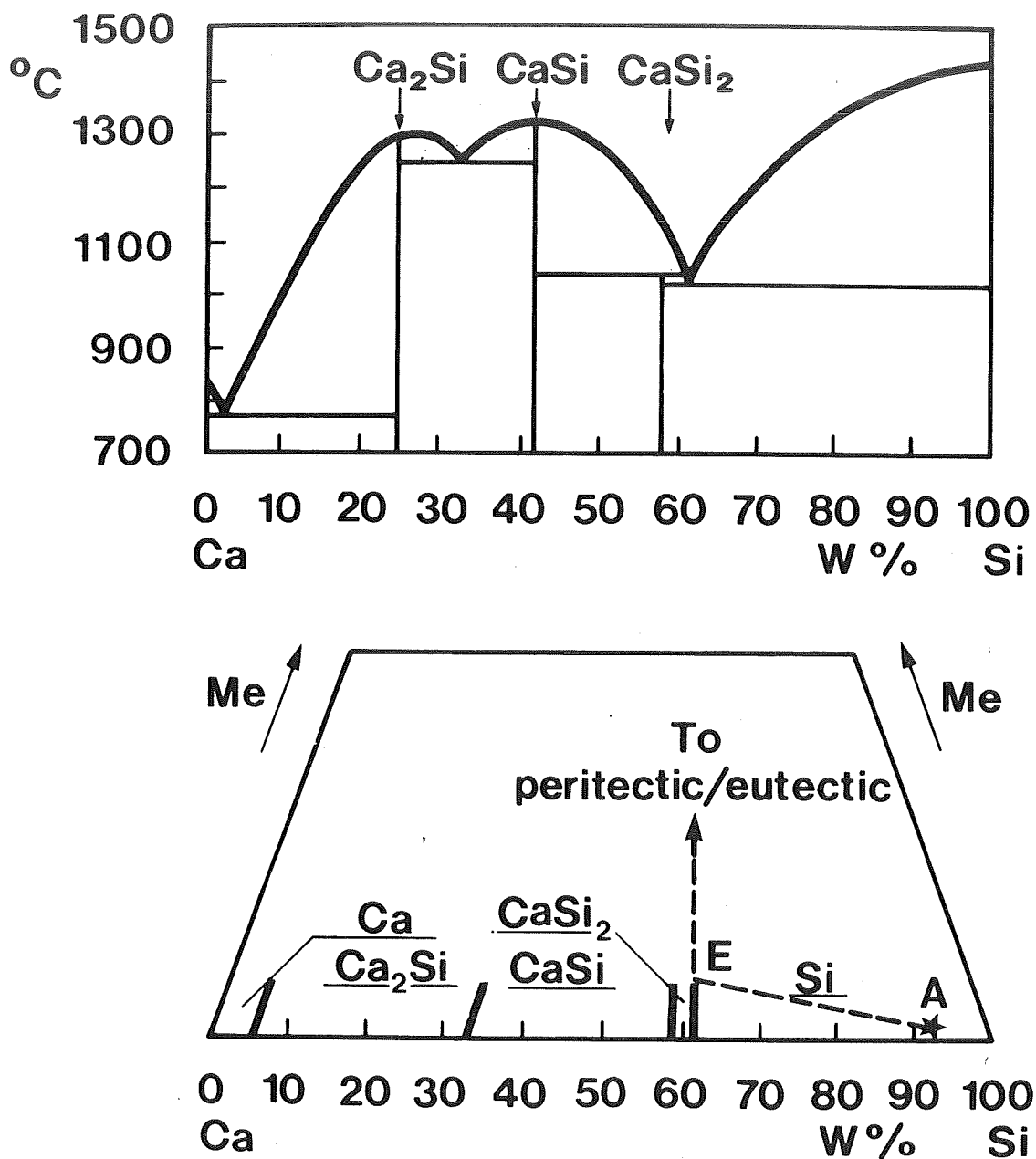
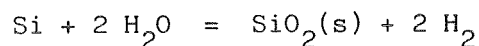


Figure 3.
The phase diagram for the system Ca-Si [5] and Ca-Si-Me (Me - an impurity element, e.g. Fe, Al, Ti).

break up exposing new surfaces of calcium disilicide for attack. This leaves free, fairly pure silicon crystals and a fine-grained silicon-containing substance that is easily removed by washing. Some small impurity crystals attached to the surface of the silicon grains, are removed by hydrofluoric acid treatment.

The leaching is based upon the fact that silicon is insoluble in acids, while the impurity phases are soluble. The insolubility of silicon must have kinetic reasons, since a thermochemical calculation indicates that silicon should be readily soluble:



$$\Delta G^\circ(298\text{K}) = -310 \text{ kJ}$$

The impurity phases dissolve irreversibly. This is important from a practical point of view, since rather impure chemicals can be used for leaching.

The leaching treatment will remove only impurities that occur as accessible separate phases. After leaching, the silicon will contain two types of impurities:

- o Impurities in solid solution in the silicon crystals
- o Impurity-containing particles engulfed in the silicon crystals

The trapped impurity particles are separate phases that will occur rather erratically in the silicon crystals. The impurities in solid solution, in contrast, result from a fairly well-defined distribution between two phases, and they should be expected to behave quite regularly.

Theoretical expectations

The aim of this theoretical discussion is to establish an ideal model for use as an indication of the potential of the process and as a scale for the evaluation of the practical results. The model is based on the classical theory of solidification [6]. This theory is rather crude and cannot be expected to give better than an order-of-magnitude agreement with experiment.

During solidification an element Me will be distributed between the silicon crystals and the melt. This distribution is described fairly well by the equation

$$\frac{c}{c_1} = k \quad (4)$$

where c and c_1 are the Me content of solid and respectively liquid silicon in contact and k is the distribution coefficient. This k is fairly constant for low contents of most elements in silicon. An equilibrium value k_0 can in principle be read from the phase diagram Me-Si, but the observed value will also depend on the kinetic conditions during solidification. Some examples of k_0 values are given in Table 1. All the elements, except possibly oxygen, have a distribution coefficient less than 1, that is, second elements will be rejected from the crystal and concentrate in the melt. These k_0 values have been determined in the pure system Me-Si. In the leaching alloy the added calcium will change the conditions. The situation is rather complicated with several effects that can influence the value of k . Considering these uncertainties, the k_0 values are accepted as reasonable first estimates for the most favourable k values that can be expected in industrial solidification of the leaching alloy.

Table 1.

Equilibrium values k_0 of the distribution coefficient for some elements in silicon [7].

Me	k_0	Me	k_0	Me	k_0
Al ¹⁾	$2 \cdot 10^{-3}$	Cu	$4 \cdot 10^{-4}$	O ¹⁾	1.4
As	0.3	Fe	$8 \cdot 10^{-6}$	P	$0.35 \cdot 10^{-5}$
Au	$2 \cdot 10^{-5}$	Ge	0.33	S	10^{-2}
B	0.8	Mg	$2 \cdot 10^{-3}$	Sn	$2 \cdot 10^{-2}$
C	$8 \cdot 10^{-2}$	Mn	10^{-5}	Ta	10^{-7}
Co	$8 \cdot 10^{-6}$	Na	$2 \cdot 10^{-3}$	Ti	10^{-5}
Cr	10^{-5}	Ni	10^{-4}	V	10^{-5}

1) Newer values: $k = 0.03$ for Al [8], $k = 0.25$ for O [9]

It is then assumed that the overall solidification of the leaching alloy is described by the wellknown solidification equation

$$c = k c_0 (1-g)^{k-1} \quad (5)$$

where

c_0 is the overall concentration of Me in the leaching alloy
 g is the solidified part of the total amount of leaching alloy

This equation is based upon three assumptions:

- o There is no diffusion in the solid
- o There is complete mixing in the liquid
- o The equation $k = c/c_1$ is true with constant k

These assumptions are believed to be fairly true for reasonable solidification conditions. The mean Me content of the silicon crystals is then

$$\bar{c} = \frac{1}{g} \int_0^g k c_0 (1-g)^{k-1} dg = \frac{c_0}{g} (1-(1-g)^k) \quad (6)$$

For the leaching process it is reasonable to assume that all the silicon crystallized before the coprecipitation of calcium disilicide is recovered, while the remainder of the alloy is lost during leaching. With low Me content, the Ca-Si phase diagram describes the amounts of silicon crystals fairly well (Figure 3). The eutectic calcium content is 39 weight per cent, and if the overall calcium content of the leaching alloy is x weight per cent, the lever rule gives the recovery R of silicon crystals

$$R \cdot x = (1-R) \cdot (39-x)$$

$$R = 1 - 0.0256 x \quad (7)$$

Here the recovery is defined as

$$R = \frac{\text{weight of crystals recovered}}{\text{total weight of leaching alloy}}$$

For the solidification of the leaching alloy, R is equal to g in the solidification equations (5) and (6) just before the start of eutectic crystallization. The mean concentration of the impurity \bar{c} can then be calculated when the content of calcium is known.

The impurity content is calculated as the ratio \bar{c}/kc_0 for several values of k in Figure 4. (This ratio is chosen as an indicator of purification because it gives the mean concentration as a factor times the readily calculable concentration in the first silicon to crystallize). The formulas and the graphs demonstrate some important properties of the leaching operation, as discussed below.

In practical operation one needs a certain amount of the calcium disilicide phase to obtain sufficient disintegration and separation of the crystals. For the high purity silicon one will probably prefer an R value as low as 0.95.

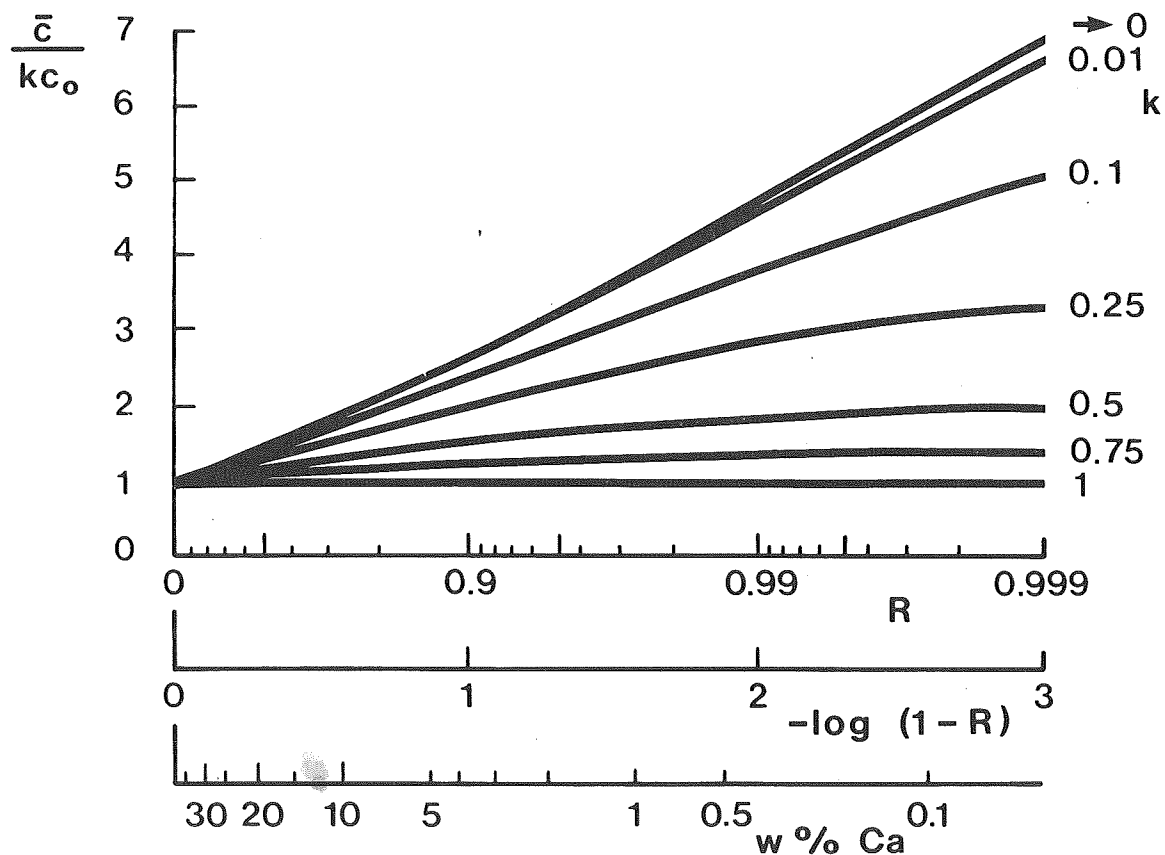


Figure 4.
Mean content \bar{c} of an impurity in silicon crystals.

Figure 4 then shows that $\bar{c}/c_0 \sim 3$ for elements with $k \leq 0.01$, that is, for most impurities. This gives the rule-of-thumb that the mean impurity concentration of the leached silicon is three times the concentration of the first silicon to precipitate. The removal of an impurity with a high distribution coefficient is modest, as shown by a calculation for phosphorus and boron:

$$\text{P: } k = 0.35, \quad \bar{c}/c_0 = 0.68$$

$$\text{B: } k = 0.80, \quad \bar{c}/c_0 = 0.95$$

For all impurities the concentration in the product is directly proportional to the concentration in the leaching alloy, as shown by equation (6). The impurity content is relatively insensitive to the value of R in the range of practical interest. Thus, if R is increased from 0.9 to 0.99, the ratio \bar{c}/c_0 is less than doubled. Therefore, the value of R , and with that the content of calcium in the leaching alloy, is chosen mainly with the aim of obtaining the correct crystallization sequence and complete disintegration. Also, the moderate sensitivity of \bar{c}/c_0 to R shows that the purifying effect of dissolving the outer layers of the silicon crystals will be moderate. However, impurities attached to the crystal surfaces may justify additional treatment.

Experimental results

The impurities should occur at a concentration less than ten ppmw in the leached solar silicon. With the available analytical equipment it was impossible to obtain reliable determinations in this range. Any result less than about 5 ppmw could indicate that the true value may be close to zero. Therefore only experiments with a rather impure leaching alloy can give results for the testing of the calculations of the previous paragraph, and only the most abundant elements, aluminium and iron, can be considered with some certainty.

The results from one experiment are shown in Table 2. The agreement between measured and calculated values is poor for iron. For aluminium the measured values fall within the area of uncertainty of the distribution coefficient. A conceivable interpretation of the high iron content is that most of the

Table 2.
Experimental and calculated results from leaching experiments

	Impurities, ppmw		
	Fe	Al	Ca
Leaching alloy	3600	3700	29000
Leached product			
Experimental	17	150	200
Calculated			
Old k value	0.1	19	
New k value		300	

} Table 1

iron occurs in inclusions that have been formed by trapping of melt during solidification. This melt, especially towards the end of the solidification, will be quite rich in impurities, and even minute quantities may increase the overall impurity content. For the present experiment it is calculated in Table 3 that an inclusion content of 850 ppm volume can explain the total iron content of the silicon. An inclusion containing 850 ppm volume is rather modest, and the qualitative impression from several micrographs is that this amount of inclusions may well occur in the grains. The contribution of aluminium from the inclusions should be close to the content of iron, but this is small compared to the amount dissolved in silicon. Thus, the content of aluminium has the correct order of magnitude, and the deviation of the iron content may be explained by the occurrence of inclusions. Therefore it is concluded that the classical theory of solidification gives a fairly good description of the impurity content of the silicon crystals.

The minor elements in the leaching alloy, as e.g. titanium, manganese, vanadium and zirconium, will occur with a content of less than 10 ppmw. From the solidification mechanism they are expected to have a content proportional to the iron content in the inclusions. The overall contents of these elements are calculated in Table 4. Because of the inclusions it is impossible to reach the low potential content of the minor elements. Some of these elements are very important when the silicon is intended for crystalline solar cells, especially if the silicon is to be crystallized as ribbons where there is no purification during the crystallization. Preferably, electrically active elements, such as titanium, vanadium and tungsten, should be in the sub-ppb range in the final solar cell.

The effect of leaching on the content of boron and phosphorus is shown in Table 5. The phosphorus removal seems to be slightly better than calculated. That may not be significant, as the range of results is close to the limit of detection of the analytical method. But a high phosphorus removal should not be surprising, since calcium has a strong affinity for phosphorus and might influence the distribution between the two phases.

Table 3.

The iron content of leached silicon interpreted as inclusions.

Leaching alloy	3600 ppmw Fe
Fe content of melt at eutectic: $c_0/(1-R)$	48000 "
Mean Fe content of inclusions, estimated	20000 "
Mean Fe content of crystals with inclusions	17 ppmw Fe
Volume content v of inclusions to explain all the Fe content ($20000 v = 17$)	850 ppmv "
(Density of Si \sim Density of Fe-containing melt)	

Table 4.
Calculated content of minor impurities of silicon grains

Impurity content(ppmw)	
Leaching alloy	Product
200 ppmw	$(200000 \cdot 17/3600) = 944$ ppbw
100 "	472 "
10 "	47 "
1 "	5 "

Table 5.
Effect of leaching on boron and phosphorus content

Sample	Element	Before leaching	After leaching	
			Experimental	Calculated
A	B ppma	1.8	1.8	1.7
B		2.6	3.1	2.5
C		2.0	2.0	1.9
D		2.1	1.5	2.0
E		2.0	2.0	1.9
F		2.4	2.5	2.3
Mean		2.15	2.15	2.04
A	P ppma	4.2	0.5	2.7
B		2.7	1.3	1.8
C		2.5	1.3	1.6
D		4.2	0.9	2.7
E		4.2	2.0	2.7
F		9.3	4.5	6.0
Mean		4.52	1.75	2.94

Some additional results are given in Table 6. The aluminium content is changed by a factor of slightly below 0.1. According to the rule-of-thumb discussed above, one should expect a factor $3k = 0.09$ when the newer value $k = 0.03$ is used. The results are close to the expectation.

Table 6.
Examples of leaching

		Impurities(ppmw)			
		Fe	Al	Ca	Ti
High Al	Before leaching	60	5000	11200	10
	After	4	360	500	1
Medium Al	Before leaching	70	660	7500	10
	After "	3	50	280	1
Low Al	Before leaching	52	140	11000	10
	After "	2	10	280	1

CALCIUM AND CARBON

Calcium and carbon are added voluntarily during the process, but they are impurities in the final product and have to be removed as far as possible. Calcium has a retrograde solubility in silicon with a maximum calcium content of 100 ppmw [10]. The mean concentration of calcium dissolved in the crystal should be less than 100 ppmw, but inclusions can increase this amount strongly. The calcium content may be reduced by remelting the crystals and e.g. treating the melt with chlorine, maybe to about 10 ppmw.

The carbon content is high during production in the submerged arc furnace. The silicon is in contact with silicon carbide and to a lesser extent silica at a temperature around 2000°C. Silicon should therefore be close to saturation at that temperature. When the silicon is cooled, dissolved carbon precipitates as silicon carbide. However, many particles are small and will sink slowly in the melt, and analysis of samples will show a carbon content higher than the true content of the melt after cooling. The analysis of rapidly cooled samples should therefore be quite close to the carbon solubility at the furnace temperature.

The solubility of carbon in molten silicon is poorly established experimentally, as pointed out in a recent review [11]. However, the measurements given the highest credibility in this review, indicate a far too high carbon solubility to fit with the experience from the carbothermic smelting of silicon. Silicon tapped directly from the submerged arc furnace contains 0.1 - 0.2 weight per cent carbon. This is in fairly good agreement with the solubility measurements of Scace and Slack [12], reproduced in Figure 5. The experimental values in this paper fall well on a straight line in a log c versus 1/T diagram, indicating good consistency of the experimental work. Therefore, at present these values are accepted as the most reliable estimate of carbon solubility.

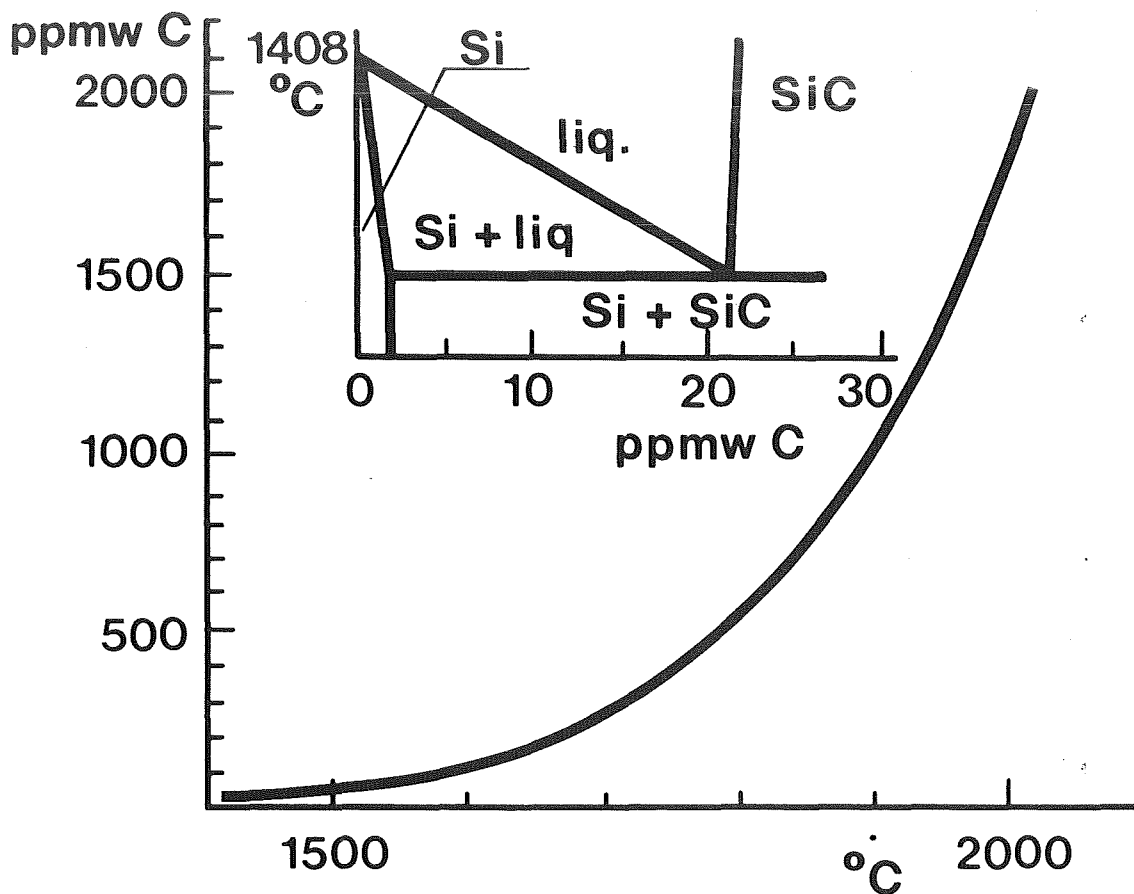


Figure 5.

The solubility of carbon in silicon. (Solubility in liquid silicon from [12], distribution coefficient 0.07 from [13])

The molten silicon cools during and after tapping, and the precipitated silicon carbide is partly trapped by the slag and at the ladle lining during melt treatment. It is difficult to remove all the precipitated silicon carbide, and the cast silicon will as a rule contain more carbon than the value read from the solubility curve at the temperature of the ladle treatment. According to practical experience, the carbon content may be reduced to some 100 ppmw in the ladle. The solubility of carbon in solid silicon near the melting point is around 4 ppmw, and any excess of this value is present as a supersaturated solid solution or as silicon carbide particles in the solidified leaching alloy. This silicon carbide will not be removed by the leaching unless the particles are completely surrounded by the calcium disilicide phase.

In the calculation of the recovery of the leaching process it was assumed that silicon was the only solid phase. Because of the precipitation of silicon carbide during the entire solidification, this assumption is not strictly true. But the amount of carbon is so low that the calculation is not invalidated.

POTENTIAL OF THE PROCESS

As shown above it is possible to estimate the final purity of the product fairly well from a simple theory of the distribution of the impurities during crystallization. Very low impurity contents can be obtained. In principle the product may be improved further by remelting and releaching several times. According to the calculations above, this can give extremely low impurity contents. Exceptions are boron, phosphorus and aluminium, which all have unfavourable distribution coefficients, and calcium, which is added in each remelting. In practical operation, however, the remelting will add impurities, and a steady state will be reached where addition balances removal. More work is necessary to evaluate this possibility.

An important contribution to the overall impurity is melt inclusions in the crystals during solidification. The calculated contents of most metals show strong improvements when the inclusions are avoided. An impurity in a class by itself is calcium, which results from the use of calcium as auxiliary element in each step. In principle calcium could be left out, at least in the last of repeated leachings, but then it would be necessary to grind the leaching alloy finely. This would complicate the aftertreatment of the leached grains, and small, slowly dissolving impurity particles would not be washed away easily.

An estimate of attainable impurity levels is given in Table 7. The intention was to produce a silicon that could be used for solar cells after a crystallization step of the Czochralski or Bridgman type, where the content of metallic impurities and carbon would be strongly reduced. This intention has been fulfilled. The Bridgman-crystallized silicon gave solar cells with an efficiency in the modul up to 13 per cent. This compares favourably with the 14 per cent value typical for high quality production-size Czochralski cells in the photovoltaic industry [14].

Table 7.
Anticipated impurity contents of high purity silicon produced by leaching

Elements	Impurities (ppmw)		
	Present technique	Without inclusions	Repeated leachings
Boron	< 1	< 1	< 1
Phosphorus	< 1	< 1	< 1
Calcium ¹⁾	< 10	< 10	< 10 ⁻³
Aluminium	< 10	< 1	< 10 ⁻³
Metals except calcium and aluminium	< 10	< 10 ⁻³	< 10 ⁻⁶
Carbon	< 50(?)	< 5	< 1

1) Remelting and calcium removal, untreated grains would contain 100 ppmw Ca without inclusions.

If the anticipated impurity contents without inclusions or for repeated leachings can be realized, the silicon can be used even for a ribbon-type wafer production where there is essentially no purification during crystallization.

The purity of the product is determined during the solidification. This purity may not be obtained because of poor leaching, but the potential for purity is set when the alloy is solidified. The leaching process is thus really a purification by crystallization with a purifying efficiency similar to the unidirectional solidification technique, and these two techniques are to be compared. In unidirectional solidification at most a few hundred kilograms can be treated in each batch, and the crystallization parameters are very critical. One has to use a rather low cooling rate to avoid constitutional supercooling, which will seriously decrease the efficiency of the purification. The separation of the pure and the impure fractions requires time-consuming manual work. For the leaching process, in contrast, even rather crude cooling gives fairly good leaching results, and both the solidification and the leaching can be adapted to large scale automated operation.

The cost of the silicon will depend strongly on the scale of the production, especially for the carbothermic step. The cost of the leaching alloy will drop rapidly with the scale up to a few thousand tons per year, and then flatten out. The cost of the leaching procedure will be less dependent on the scale. It is premature to give exact cost information before the details of the procedure have been fixed. It can be claimed, however, that for a production of several thousand tons a year, the cost of production will be only a few times the cost of ordinary metallurgical silicon.

ACKNOWLEDGEMENT

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DISCUSSION

AULICH: Would you comment on your carbon removal technique and why you believe that repeated leaching will reduce the carbon content?

SCHEI: As you explained in your paper, you have used crystallization to remove carbon. In our experiments, it seems that small silicon-carbide particles are not always engulfed in growing silicon crystals, so we have the hope of removing them and containing them in the calcium disilicide. If we are below the solubility limits, it will be a normal precipitation procedure.

SCHMID: You mentioned in your paper that the silicon carbide concentration was reduced by the ladle treatment. What type of treatment is used?

SCHEI: That's mainly a mechanical procedure. Silicon carbide tends to stick to the slag and the lining of the ladle and, also, if it spends some time in the ladle, the large, heavier particles will sink. The solidification can be improved by blowing with a gas, and we also have the option of filtering.

WRIGHT: At Solarex, we confirmed that a gas extraction technique was very effective in removing silicon carbide. Using a directional solidification technique, we didn't find that particles below 10 μm tended to be within the solidified structure. We weren't growing single crystals, but polysilicon. The silicon carbide particles were actually within the crystal and not at the grain boundaries, and we didn't get a significant reduction in silicon carbide particles by a directional solidification process.

KOINUMA: I would like to ask about the effects of leaching on the boron and phosphorus levels. I think you mentioned that the boron and phosphorus levels were not reduced very much by leaching, but Dr. Aulich mentioned that the levels could be reduced considerably by leaching of the silica. I wonder why there are these differences between the silica and silicon leaching.

SCHEI: Well, these are two completely different processes. I don't know much about the leaching of silica, but it has been well known for many years that crucibles of quartz are made from a boron containing material and the boron is leached out. We do not have the same distribution problems as in that system.

AULICH: I would like to comment on this question. Two different materials are being considered. On the one hand, there is silicon and it is leached. On the other hand, glass fibers are processed. The processes are not the same.